P. ,ENT COOPERATION TREA . .

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

United States Patent and Trademark Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 16 July 1999 (16.07.99)	
International application No. PCT/GB98/03582	**Applicant's or agent's file reference** DWS/VV/P250WO
International filing date (day/month/year) 03 December 1998 (03.12.98)	**Priority date** (day/month/year) 04 December 1997 (04.12.97)
Applicant TUCK, Richard, Allan et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

25 June 1999 (25.06.99)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was
[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer S. Mafla Telephone No.: (41-22) 338.83.38

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference DWS/VV/P250WO	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB98/03582	International filing date *(day/month/year)* 03/12/1998	Priority date *(day/month/year)* 04/12/1997
International Patent Classification (IPC) or national classification and IPC H01J1/30		
Applicant PRINTABLE FIELD EMITTERS LIMITED et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 14 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
25/06/1999	03.03.00
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Colvin, G Telephone No. +31 70 340 2864

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB98/03582

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-4,7-11,13-29	as originally filed			
5,6,12,30,31	as received on	14/01/2000	with letter of	10/01/2000

Claims, No.:

1-59	as received on	14/01/2000	with letter of	10/01/2000

Drawings, sheets:

1/13-13/13	as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-59
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-59
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-59
	No:	Claims	

2. Citations and explanations

see separate sheet

INTERNATIONAL PRELIMINARY EXAMINATION REPORT - SEPARATE SHEET

International application No. PCT/GB98/03582

<u>**Re Item V**</u>

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following document:

D3: WO-A-97/06549 [Tuck et al.] - cited in application

2.1 Claim 1 discloses a method of forming a field electron emission material. Such materials are known in the prior art (see D3). The process steps according to claim 1 and evident in D3 comprise disposing on a substrate having electrical conductive surface a plurality of electrically conductive particles, each with a layer of electrically insulating material disposed either in a first location between said conductive surface and said particle, or in a second location between said particle and the environment in which the field electron emission material is disposed (see fig.3 of D3).

In addition, claim 1 discloses the steps of ensuring that the electrically insulating material is not deposited at both the first and second locations and that the particles form electron emission sites at said first or second locations where said electrically insulating material is disposed. These steps are not known from D3, hence the subject-matter of claim 1 is novel (Article 33(2) PCT).

The problem solved by these novel process steps is to produce an emitter achieving metal-insulator-vacuum emission in a controlled manner. The novel steps of claim 1 for achieving this are not obvious with respect to the known prior art, thus the subject-matter of claim 1 appears to involve an inventive step (Article 33(3) PCT).

2.2 Claims 2-35 disclose process steps additional to those of claim 1 and hence the subject-matter of these claims is likewise novel and inventive.

2.3 Claim 36 discloses a field electron emission material produced by the method according to claim 1. No prior art electron emission material is known to have the

structure resulting from the steps of claim 1. For example, even though D3 discloses a field electron emission material where emission occurs at the interface between particle and an electrically insulating material, it should be noted that the insulating material is disposed at both the first and second locations, contrary to the features of claim 36. Nor is it obvious to exclude one or the other locations. Hence the subject-matter of claim 36 is both novel and inventive.

Claims 37-59 disclose features additional to those of claim 36 and hence the subject-matter of these claims is likewise novel and inventive.

Latham and Mousa (*J. Phys.D: Appl. Phys. 19, pp 699-713 (1986)*) describe composite metal-insulator tip-based emitters using the above hot electron process and in 1988 S Bajic and R V Latham, (*Journal of Physics D Applied Physics, vol. 21 200-204 (1988)*), described a composite that created a high density of metal-insulator-metal-insulator-vacuum (MIMIV) emitting sites. The composite had conducting particles dispersed in an epoxy resin. The coating was applied to the surface by standard spin coating techniques.

Much later in 1995 Tuck, Taylor and Latham (*GB 2304989*) improved the above MIMIV emitter by replacing the epoxy resin with an inorganic insulator that both improved stability and enabled it to be operated in sealed off vacuum devices.

All of the inventions described above rely on hot electron field emission of the type responsible for pre-breakdown currents but, so far, no method has yet been proposed to produce emitters with a plurality of conducting particle MIV emitters in a controlled manner.

Preferred embodiments of the present invention aim to provide cost effective broad area field emitting materials and devices. The materials may be used in devices that include: field electron emission display panels; high power pulse devices such as electron MASERS and gyrotrons; crossed-field microwave tubes such as CFAs; linear beam tubes such as klystrons; flash x-ray tubes; triggered spark gaps and related devices; broad area x-ray sources for sterilisation; vacuum gauges; ion thrusters for space vehicles; particle accelerators; ozonisers; and plasma reactors.

According to a first aspect of the present invention there is provided a method of forming a field electron emission material, comprising the step of disposing on a substrate having an electrically

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conductive surface a plurality of electrically conductive particles, each with a layer of electrically insulating material disposed either in a first location between said conductive surface and said particle, or in a second location between said particle and the environment in which the field electron emission material is disposed, but not in both of said first and second locations, such that at least some of said particles form electron emission sites at said first or second locations where said electrically insulating material is disposed.

Thus, in preferred embodiments of the invention, an emitter may be formed so that a MIV channel is either at the base or the top of the particle. If the MIV channel is at the base, as in Figure 1a, the antenna effect enhances the electric field across the channel according to the ratio of particle height normal to the surface and insulator thickness. However, it is equally possible to form a MIV channel on the top of the particle by overcoating a particle in electrical contact with the surface with an insulating layer. In this case the field enhancement is based upon the particle shape. For all reasonable particle shapes, one will typically be limited to a field enhancement factor of approximately ten. The arrangement with the lower channel will usually give the lowest switch-on field. The arrangement with the channel on top can be far more robust and would find application in pulsed power devices where high electric fields and large electrostatic forces are the norm and very high current densities are required.

Preferably the dimension of said particles normal to the surface of the conductor is significantly greater than the thickness of said layer of insulating material.

Preferably, said dimension substantially normal to the surface of said particle is at least 10 times greater than said thickness.

A field electron emission device as above may comprise a display device.

A field electron emission device as above may comprise a lamp.

Preferably, said lamp is substantially flat.

A field electron emission device as above may comprise an electrode plate supported on insulating spacers in the form of a cross-shaped structure.

The field electron emission material may be applied in patches which are connected in use to an applied cathode voltage via a resistor.

Preferably, said resistor is applied as a resistive pad under each emitting patch.

A respective said resistive pad may be provided under each emitting patch, such that the area of each such resistive pad is greater than that of the respective emitting patch.

Preferably, said emitter material and/or a phosphor is/are disposed upon one or more one-dimensional array of conductive tracks which are arranged to be addressed by electronic driving means so as to produce a scanning illuminated line.

Such a field electron emission device may include said electronic driving means.

The environment may be gaseous, liquid, solid, or a vacuum.

A field electron emission device as above may include a gettering material within the device.

requirements of the invention - for example, by aligning such particulates, making them of sufficient size and density, etc. In the manufacture of thin-film diamond, the trend in the art has been emphatically to minimise graphite inclusions, whereas, in appropriate embodiments of the invention, such surface particulates are deliberately included and carefully engineered.

An important feature of some embodiments of the invention is the ability to print an emitting pattern, thus enabling complex multi-emitter patterns, such as those required for displays, to be created at modest cost. Furthermore, the ability to print enables low-cost substrate materials, such as glass to be used; whereas micro-engineered structures are typically built on high-cost single crystal substrates. In the context of this specification, printing means a process that places or forms an emitting material in a defined pattern. Examples of suitable processes are: screen printing, Xerography, photolithography, electrostatic deposition, spraying or offset lithography.

Devices that embody the invention may be made in all sizes, large and small. This applies especially to displays, which may range from a single pixel device to a multi-pixel device, from miniature to macro-size displays.

In this specification, by a "channel" or "conducting channel", we mean a region of an insulator where its properties have been locally modified – for example, by some forming process. In the example of a conductor-insulator-vacuum (e.g. MIV) structure, such a modification facilitates the transport of electrons from the back contact (between conductor/electrode and insulator), through the insulator into the vacuum. In the example of a conductor-insulator-conductor (e.g. MIM) structure,

such a modification facilitates the transport of electrons from the back contact, through the insulator to the other conductor/electrode.

In this specification, the verb "comprise" has its normal dictionary meaning, to denote non-exclusive inclusion. That is, use of the word "comprise" (or any of its derivatives) to include one feature or more, does not exclude the possibility of also including further features.

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CLAIMS

1. A method of forming a field electron emission material, comprising the step of disposing on a substrate having an electrically conductive surface a plurality of electrically conductive particles, each with a layer of electrically insulating material disposed either in a first location between said conductive surface and said particle, or in a second location between said particle and the environment in which the field electron emission material is disposed, but not in both of said first and second locations, such that at least some of said particles form electron emission sites at said first or second locations where said electrically insulating material is disposed.

2. A method according to claim 1, wherein the dimension of said particles normal to the surface of the conductor is significantly greater than the thickness of said layer of insulating material.

3. A method according to claim 2, wherein said dimension substantially normal to the surface of said particle is at least 10 times greater than said thickness.

4. A method according to claim 3, wherein said dimension substantially normal to the surface of said particle is at least 100 times greater than each said thickness.

5. A method according to any of claims 1 to 4, wherein the thickness of said insulating material is in the range 10 nm to 100 nm (100 Å to 1000 Å) and said particle dimension is in the range 1μm to 10 μm.

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6. A method according to any of claims 1 to 5, wherein there is provided a substantially single layer of said conductive particles each having their dimension substantially normal to the surface in the range 0.1 μm to 400 μm.

7. A method according to any of the preceding claims, wherein said insulating material comprises a material other than diamond.

8. A method according to any of the preceding claims, wherein said insulating material is an inorganic material.

9. A method according to any of the preceding claims, wherein said insulating material comprises a glass, lead based glass, glass ceramic, melted glass or other glassy material, ceramic, oxide ceramic, oxidised surface, nitride, nitrided surface, boride ceramic, diamond, diamond-like carbon or tetragonal amorphous carbon.

10. A method according to any of the preceding claims, wherein each said electrically conductive particle is substantially symmetrical.

11. A method according to any of the preceding claims, wherein each said electrically conductive particle is of substantially rough-hewn cuboid shape.

12. A method according to any of claims 1 to 10, wherein each said electrically conductive particle is of substantially spheroid shape with a textured surface.

13. A method according to any of claims 1 to 11, wherein said conductive particles each have a longest dimension and are preferentially aligned with their longest dimension substantially normal to the substrate.

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14. A method according to any of the preceding claims, wherein said conductive particles having a mutual spacing, centre-to-centre, of at least 1.8 times their smallest dimension.

15. A method according to any of the preceding claims, wherein each said particle is, or at least some of said particles are, selected from the group comprising metals, semiconductors, electrical conductors, graphite, silicon carbide, tantalum carbide, hafnium carbide, zirconium carbide, boron carbide, titanium diboride, titanium carbide, titanium carbonitride, the Magneli sub-oxides of titanium, semi-conducting silicon, III-V compounds and II-VI compounds.

16. A method according to any of the preceding claims, wherein each said particle, or at least some of said particles, are only partially covered in said insulating material, and each such particle comprises a gettering material.

17. A method according to any of the preceding claims, wherein said surface is coated with said particles by means of an ink containing said particles and said insulating material to form said insulating layer, the properties of said ink being such that said particles have portions which are caused to project from said insulating material, uncoated by the insulating material, as a result of the coating process.

18. A method according to claim 17, wherein said ink is applied to said electrically conductive surface by a printing process.

19. A method according to any of the preceding claims, wherein said electrically conductive particles and/or electrically insulating material are applied to said electrically conductive substrate in a photosensitive binder to permit later patterning.

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20. A method according to any of the preceding claims, wherein said insulating material is formed by the step of fusing, sintering or otherwise joining together a mixture of particles or *in situ* chemical reaction.

21. A method according to claim 20, wherein the insulating material comprises a glass, glass ceramic, ceramic, oxide ceramic, oxide, nitride, boride, diamond, polymer or resin.

22. A method according to any of the preceding claims, wherein each said electrically conductive particle comprises a fibre chopped into a length longer than its diameter.

23. A method according to any of claims 1 to 21, wherein said particles are formed by the deposition of a conducting layer upon said insulating layer and subsequent patterning, either by selective etching or masking, to form isolated islands that function as said particles.

24. A method according to any of claims 1 to 21, wherein said particles are applied to said conductive surface by a spraying process.

25. A method according to any of claims 1 to 21, wherein said conductive particles are formed by depositing a layer that subsequently crazes, or is caused to craze, into substantially electrically isolated raised flakes.

26. A method according to claim 23, 24 or 25, wherein said conducting layer comprises a metal, conducting element or compound, semiconductor or composite.

27. A method according to any of the preceding claims, wherein the distribution of said sites over the field electron emission material is random.

28. A method according to any of the preceding claims, wherein said sites are distributed over the field electron emission material at an average density of at least 10^2 cm^{-2}.

29. A method according to any of the preceding claims, wherein said sites are distributed over the field electron emission material at an average density of at least 10^3 cm^{-2}, 10^4 cm^{-2} or10^5 cm^{-2}.

30. A method according to any of the preceding claims, wherein the distribution of said sites over the field electron emission material is substantially uniform.

31. A method according to claim 30, wherein the distribution of said sites over the field electron emission material has a uniformity such that the density of said sites in any circular area of 1mm diameter does not vary by more than 20% from the average density of distribution of sites for all of the field electron emission material.

32. A method according to claim 30, wherein the distribution of said sites over the field electron emission material when using a circular measurement area of 1 mm in diameter is substantially Binomial or Poisson.

33. A method according to claim 30, wherein the distribution of said sites over the field electron emission material has a uniformity such that there is at least a 50% probability of at least one emitting site being located in any circular area of 4 μm diameter.

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34. A method according to claim 30, wherein the distribution of said sites over the field electron emission material has a uniformity such that there is at least a 50% probability of at least one emitting site being located in any circular area of 10 μm diameter.

35. A method according to any of the preceding claims, including the preliminary step of classifying said particles by passing a liquid containing particles through a settling tank in which particles over a predetermined size settle such that liquid output from said tank contains particles which are less than said predetermined size and which are then coated on said substrate.

36. A field electron emission material produced by a method according to any of the preceding claims.

37. A field electron emission device comprising a field electron emission material according to claim 36 and means for subjecting said material to an electric field in order to cause said material to emit electrons.

38. A field electron emission device according to claim 37, comprising a substrate with an array of emitter patches of said field electron emission material, and control electrodes with aligned arrays of apertures, which electrodes are supported above the emitter patches by insulating layers.

39. A field electron emission device according to claim 38, wherein said apertures are in the form of slots.

40. A field electron emission device according to any of claims 37 to 39, comprising a plasma reactor, corona discharge device, silent

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discharge device, ozoniser, an electron source, electron gun, electron device, x-ray tube, vacuum gauge, gas filled device or ion thruster.

41. A field electron emission device according to any of claims 37 to 40, wherein the field electron emission material supplies the total current for operation of the device.

42. A field electron emission device according to any of claims 37 to 40, wherein the field electron emission material supplies a starting, triggering or priming current for the device.

43. A field electron emission device according to any of claims 37 to 42, comprising a display device.

44. A field electron emission device according to any of claims 37 to 42, comprising a lamp.

45. A field electron emission device according to claim 44, wherein said lamp is substantially flat.

46. A field electron emission device according to any of claims 37 to 45, comprising an electrode plate supported on insulating spacers in the form of a cross-shaped structure.

47. A field electron emission device according to any of claims 37 to 46, wherein, the field electron emission material is applied in patches which are connected in use to an applied cathode voltage via a resistor.

48. A field electron emission device according to claim 47, wherein said resistor is applied as a resistive pad under each emitting patch.

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49. A field electron emission device according to claim 48, wherein a respective said resistive pad is provided under each emitting patch, such that the area of each such resistive pad is greater than that of the respective emitting patch.

50. A field electron emission device according to any of claims 37 to 49, wherein said emitter material and/or a phosphor is/are disposed upon one or more one-dimensional array of conductive tracks which are arranged to be addressed by electronic driving means so as to produce a scanning illuminated line.

51. A field electron emission device according to claim 50, including said electronic driving means.

52. A field electron emission device according to any of claims 37 to 51, wherein said environment is gaseous, liquid, solid, or a vacuum.

53. A field electron emission device according to any of claims 37 to 52, including a gettering material within the device.

54. A field electron emission device according to claim 53, wherein said gettering material is affixed to an anode of the device.

55. A field electron emission device according to claim 53 or 54, wherein said gettering material may be affixed to a cathode of the device.

56. A field electron emission device according to claim 55, wherein said field electron emission material is arranged in patches, and said gettering material is disposed within said patches.

57. A field electron emission device according to claim 53, comprising an anode, a cathode, spacer sites on said anode and cathode, spacers

located at at least some of said spacer sites to space said anode from said cathode, and said gettering material located on said anode at others of said spacer sites where spacers are not located.

58. A field electron emission device according to claim 57, wherein said spacer sites are at a regular or periodic mutual spacing.

59. A field electron emission device according to any of claims 37 to 58, wherein a cathode of the device is optically translucent and so arranged in relation to an anode of the device that electrons emitted from the cathode impinge upon the anode to cause electro-luminescence at the anode, which electro-luminescence is visible through the optically translucent cathode.

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PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
DWS/VV/P250WO		
International application No. PCT/GB 98/03582	International filing date (*day/month/year*) 03/12/1998	(Earliest) Priority Date (*day/month/year*) 04/12/1997
Applicant PRINTABLE FIELD EMITTERS LIMITED et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

[ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

[ ] contained in the international application in written form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readble form.

[ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

[X] the text is approved as submitted by the applicant.

[ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

[X] the text is approved as submitted by the applicant.

[ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. 2a, 2b

[X] as suggested by the applicant.

[ ] because the applicant failed to suggest a figure.

[ ] because this figure better characterizes the invention.

[ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
/GB 98/03582

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01J1/30 H01J9/02

According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 23002 A (ADVANCED TECH MATERIALS ;SILICON VIDEO CORP (US)) 26 June 1997 see page 7, line 8 - line 11 see page 20, line 3 - line 6 see page 20, line 20 - line 32 see page 23, line 21 - page 24, line 14 see figure 5B ---	1,37,38
A	WO 91 05361 A (MOTOROLA INC) 18 April 1991 see figures 2,3 see page 4, line 28 - page 5, line 32 ---	1,37,38
A	WO 97 06549 A (TUCK RICHARD ALLAN ;LATHAM RODNEY VAUGHAN (GB); TAYLOR WILLIAM (GB) 20 February 1997 cited in the application see figures --- -/--	1,37,38

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 March 1999	31/03/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Colvin, G

1

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	BAJIC S ET AL: "ENHANCED COLD-CATHODE EMISSION USING COMPOSITE RESIN-CARBON COATINGS" JOURNAL OF PHYSICS D. APPLIED PHYSICS, vol. 21, 1988, pages 200-204, XP002017628 cited in the application see abstract; figure 5 ---	1,37,38
X	US 5 663 608 A (JONES GARY W ET AL) 2 September 1997 see figure 24 see column 15, line 65 - line 67 see column 16, line 13 - line 30 ---	1,37,38
A	XU N S ET AL: "FIELD-INDUCED ELECTRON EMISSION FROM CVD DIAMOND FILNS ON PLANAR MOSUBSTRATES" DIAMOND FILMS AND TECHNOLOGY, vol. 4, no. 4, 1 January 1994, pages 249-258, XP000561551 see figure 6 -----	1,37,38

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 98/03582

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9723002 A	26-06-1997	AU 1340397 A	14-07-1997
		EP 0868752 A	07-10-1998
WO 9105361 A	18-04-1991	US 5019003 A	28-05-1991
		AT 122500 T	15-05-1995
		AU 6432990 A	28-04-1991
		DE 69019368 D	14-06-1995
		DE 69019368 T	04-01-1996
		DK 500553 T	11-09-1995
		EP 0500553 A	02-09-1992
		ES 2073037 T	01-08-1995
		JP 5500585 T	04-02-1993
WO 9706549 A	20-02-1997	AU 6626096 A	05-03-1997
		CN 1192288 A	02-09-1998
		EP 0842526 A	20-05-1998
		GB 2304989 A,B	26-03-1997
		GB 2306246 A,B	30-04-1997
US 5663608 A	02-09-1997	US 5534743 A	09-07-1996
		EP 0780022 A	25-06-1997
		WO 9608028 A	14-03-1996
		EP 0776493 A	04-06-1997
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INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/GB 98/03582

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01J1/30 H01J9/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 23002 A (ADVANCED TECH MATERIALS ;SILICON VIDEO CORP (US)) 26 June 1997 see page 7, line 8 - line 11 see page 20, line 3 - line 6 see page 20, line 20 - line 32 see page 23, line 21 - page 24, line 14 see figure 5B ---	1,37,38
A	WO 91 05361 A (MOTOROLA INC) 18 April 1991 see figures 2,3 see page 4, line 28 - page 5, line 32 ---	1,37,38
A	WO 97 06549 A (TUCK RICHARD ALLAN ;LATHAM RODNEY VAUGHAN (GB); TAYLOR WILLIAM (GB)) 20 February 1997 cited in the application see figures --- -/--	1,37,38

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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International Application No
PCT/GB 98/03582

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 5 663 608 A (JONES GARY W ET AL) 2 September 1997 see figure 24 see column 15, line 65 - line 67 see column 16, line 13 - line 30	1,37,38
A	XU N S ET AL: "FIELD-INDUCED ELECTRON EMISSION FROM CVD DIAMOND FILNS ON PLANAR MOSUBSTRATES" DIAMOND FILMS AND TECHNOLOGY, vol. 4, no. 4, 1 January 1994, pages 249-258, XP000561551 see figure 6	1,37,38

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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ART 34 AMDT

Latham and Mousa (*J. Phys.D: Appl. Phys. 19, pp 699-713 (1986)*) describe composite metal-insulator tip-based emitters using the above hot electron process and in 1988 S Bajic and R V Latham, (*Journal of Physics D Applied Physics, vol. 21 200-204 (1988)*), described a composite that created a high density of metal-insulator-metal-insulator-vacuum (MIMIV) emitting sites. The composite had conducting particles dispersed in an epoxy resin. The coating was applied to the surface by standard spin coating techniques.

Much later in 1995 Tuck, Taylor and Latham (*GB 2304989*) improved the above MIMIV emitter by replacing the epoxy resin with an inorganic insulator that both improved stability and enabled it to be operated in sealed off vacuum devices.

All of the inventions described above rely on hot electron field emission of the type responsible for pre-breakdown currents but, so far, no method has yet been proposed to produce emitters with a plurality of conducting particle MIV emitters in a controlled manner.

Preferred embodiments of the present invention aim to provide cost effective broad area field emitting materials and devices. The materials may be used in devices that include: field electron emission display panels; high power pulse devices such as electron MASERS and gyrotrons; crossed-field microwave tubes such as CFAs; linear beam tubes such as klystrons; flash x-ray tubes; triggered spark gaps and related devices; broad area x-ray sources for sterilisation; vacuum gauges; ion thrusters for space vehicles; particle accelerators; ozonisers; and plasma reactors.

According to a first aspect of the present invention there is provided a method of forming a field electron emission material, comprising the step of coating a substrate having an electrically conductive

surface with a plurality of electrically conductive particles, each with a layer of electrically insulating material disposed either in a first location between said conductive surface and said particle, or in a second location between said particle and the environment in which the field electron emission material is disposed, but not in both of said first and second locations, such that at least some of said particles form electron emission sites at said first or second locations.

Thus, in preferred embodiments of the invention, an emitter may be formed so that a MIV channel is either at the base or the top of the particle. If the MIV channel is at the base, as in Figure 1a, the antenna effect enhances the electric field across the channel according to the ratio of particle height normal to the surface and insulator thickness. However, it is equally possible to form a MIV channel on the top of the particle by overcoating a particle in electrical contact with the surface with an insulating layer. In this case the field enhancement is based upon the particle shape. For all reasonable particle shapes, one will typically be limited to a field enhancement factor of approximately ten. The arrangement with the lower channel will usually give the lowest switch-on field. The arrangement with the channel on top can be far more robust and would find application in pulsed power devices where high electric fields and large electrostatic forces are the norm and very high current densities are required.

Preferably the dimension of said particles normal to the surface of the conductor is significantly greater than the thickness of said layer of insulating material.

Preferably, said dimension substantially normal to the surface of said particle is at least 10 times greater than said thickness.

A field electron emission device as above may comprise a display device.

A field electron emission device as above may comprise a lamp.

Preferably, said lamp is substantially flat.

A field electron emission device as above may comprise an electrode plate supported on insulating spacers in the form of a cross-shaped structure.

The field electron emission material may be applied in patches which are connected in use to an applied cathode voltage via a resistor.

Preferably, said resistor is applied as a resistive pad under each emitting patch.

A respective said resistive pad may be provided under each emitting patch, such that the area of each such resistive pad is greater than that of the respective emitting patch.

Preferably, said emitter material and/or a phosphor is/are coated upon one or more one-dimensional array of conductive tracks which are arranged to be addressed by electronic driving means so as to produce a scanning illuminated line.

Such a field electron emission device may include said electronic driving means.

The environment may be gaseous, liquid, solid, or a vacuum.

A field electron emission device as above may include a gettering material within the device.

such a modification facilitates the transport of electrons from the back contact, through the insulator to the other conductor/electrode.

In this specification, the verb "comprise" has its normal dictionary meaning, to denote non-exclusive inclusion. That is, use of the word "comprise" (or any of its derivatives) to include one feature or more, does not exclude the possibility of also including further features.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any

accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A method of forming a field electron emission material, comprising the step of coating a substrate having an electrically conductive surface with a plurality of electrically conductive particles, each with a layer of electrically insulating material disposed either in a first location between said conductive surface and said particle, or in a second location between said particle and the environment in which the field electron emission material is disposed, but not in both of said first and second locations, such that at least some of said particles form electron emission sites at said first or second locations.

2. A method according to claim 1, wherein the dimension of said particles normal to the surface of the conductor is significantly greater than the thickness of said layer of insulating material.

3. A method according to claim 2, wherein said dimension substantially normal to the surface of said particle is at least 10 times greater than said thickness.

4. A method according to claim 3, wherein said dimension substantially normal to the surface of said particle is at least 100 times greater than each said thickness.

5. A method according to any of claims 1 to 4, wherein the thickness of said insulating material is in the range 10 nm to 100 nm (100 Å to 1000 Å) and said particle dimension is in the range 1μm to 10 μm.

6. A method according to any of claims 1 to 5, wherein there is provided a substantially single layer of said conductive particles each

having their dimension substantially normal to the surface in the range 0.1 μm to 400 μm.

7. A method according to any of the preceding claims, wherein said insulating material comprises a material other than diamond.

8. A method according to any of the preceding claims, wherein said insulating material is an inorganic material.

9. A method according to any of the preceding claims, wherein said insulating material comprises a glass, lead based glass, glass ceramic, melted glass or other glassy material, ceramic, oxide ceramic, oxidised surface, nitride, nitrided surface, boride ceramic, diamond, diamond-like carbon or tetragonal amorphous carbon.

10. A method according to any of the preceding claims, wherein each said electrically conductive particle is substantially symmetrical.

11. A method according to any of the preceding claims, wherein each said electrically conductive particle is of substantially rough-hewn cuboid shape.

12. A method according to any of claims 1 to 10, wherein each said electrically conductive particle is of substantially spheroid shape with a textured surface.

13. A method according to any of claims 1 to 11, wherein said conductive particles each have a longest dimension and are preferentially aligned with their longest dimension substantially normal to the substrate.

14. A method according to any of the preceding claims, wherein said conductive particles having a mutual spacing, centre-to-centre, of at least 1.8 times their smallest dimension.

15. A method according to any of the preceding claims, wherein each said particle is, or at least some of said particles are, selected from the group comprising metals, semiconductors, electrical conductors, graphite, silicon carbide, tantalum carbide, hafnium carbide, zirconium carbide, boron carbide, titanium diboride, titanium carbide, titanium carbonitride, the Magneli sub-oxides of titanium, semi-conducting silicon, III-V compounds and II-VI compounds.

16. A method according to any of the preceding claims, wherein each said particle, or at least some of said particles, are only partially covered insaid insulating material, and each such particle comprises a gettering material.

17. A method according to any of the preceding claims, wherein said surface is coated with said particles by means of an ink containing said particles and said insulating material to form said insulating layer, the properties of said ink being such that said particles have portions which are caused to project from said insulating material, uncoated by the insulating material, as a result of the coating process.

18. A method according to claim 17, wherein said ink is applied to said electrically conductive surface by a printing process.

19. A method according to any of the preceding claims, wherein said electrically conductive particles and/or electrically insulating material are applied to said electrically conductive substrate in a photosensitive binder to permit later patterning.

20. A method according to any of the preceding claims, wherein said insulating material is formed by the step of fusing, sintering or otherwise joining together a mixture of particles or *in situ* chemical reaction.

21. A method according to claim 20, wherein the insulating material comprises a glass, glass ceramic, ceramic, oxide ceramic, oxide, nitride, boride, diamond, polymer or resin.

22. A method according to any of the preceding claims, wherein each said electrically conductive particle comprises a fibre chopped into a length longer than its diameter.

23. A method according to any of claims 1 to 21, wherein said particles are formed by the deposition of a conducting layer upon said insulating layer and subsequent patterning, either by selective etching or masking, to form isolated islands that function as said particles.

24. A method according to any of claims 1 to 21, wherein said particles are applied to said conductive surface by a spraying process.

25. A method according to any of claims 1 to 21, wherein said conductive particles are formed by depositing a layer that subsequently crazes, or is caused to craze, into substantially electrically isolated raised flakes.

26. A method according to claim 23, 24 or 25, wherein said conducting layer comprises a metal, conducting element or compound, semiconductor or composite.

27. A method according to any of the preceding claims, wherein the distribution of said sites over the field electron emission material is random.

28. A method according to any of the preceding claims, wherein said sites are distributed over the field electron emission material at an average density of at least 10^2 cm^{-2}.

29. A method according to any of the preceding claims, wherein said sites are distributed over the field electron emission material at an average density of at least 10^3 cm^{-2}, 10^4 cm^{-2} or10^5 cm^{-2}.

30. A method according to any of the preceding claims, wherein the distribution of said sites over the field electron emission material is substantially uniform.

31. A method according to claim 30, wherein the distribution of said sites over the field electron emission material has a uniformity such that the density of said sites in any circular area of 1mm diameter does not vary by more than 20% from the average density of distribution of sites for all of the field electron emission material.

32. A method according to claim 30, wherein the distribution of said sites over the field electron emission material when using a circular measurement area of 1 mm in diameter is substantially Binomial or Poisson.

33. A method according to claim 30, wherein the distribution of said sites over the field electron emission material has a uniformity such that there is at least a 50% probability of at least one emitting site being located in any circular area of 4 μm diameter.

34. A method according to claim 30, wherein the distribution of said sites over the field electron emission material has a uniformity such that there is at least a 50% probability of at least one emitting site being located in any circular area of 10 μm diameter.

35. A method according to any of the preceding claims, including the preliminary step of classifying said particles by passing a liquid containing particles through a settling tank in which particles over a predetermined size settle such that liquid output from said tank contains particles which are less than said predetermined size and which are then coated on said substrate.

36. A method of forming a field electron emission material, substantially as hereinbefore described with reference to the accompanying drawings.

37. A field electron emission material produced by a method according to any of the preceding claims.

38. A field electron emission device comprising a field electron emission material according to claim 37 and means for subjecting said material to an electric field in order to cause said material to emit electrons.

39. A field electron emission device according to claim 38, comprising a substrate with an array of emitter patches of said field electron emission material, and control electrodes with aligned arrays of apertures, which electrodes are supported above the emitter patches by insulating layers.

40. A field electron emission device according to claim 39, wherein said apertures are in the form of slots.

41. A field electron emission device according to any of claims 38 to 40, comprising a plasma reactor, corona discharge device, silent discharge device, ozoniser, an electron source, electron gun, electron device, x-ray tube, vacuum gauge, gas filled device or ion thruster.

42. A field electron emission device according to any of claims 38 to 41, wherein the field electron emission material supplies the total current for operation of the device.

43. A field electron emission device according to any of claims 38 to 41, wherein the field electron emission material supplies a starting, triggering or priming current for the device.

44. A field electron emission device according to any of claims 38 to 43, comprising a display device.

45. A field electron emission device according to any of claims 38 to 43, comprising a lamp.

46. A field electron emission device according to claim 45, wherein said lamp is substantially flat.

47. A field electron emission device according to any of claims 38 to 46, comprising an electrode plate supported on insulating spacers in the form of a cross-shaped structure.

48. A field electron emission device according to any of claims 38 to 47, wherein, the field electron emission material is applied in patches which are connected in use to an applied cathode voltage via a resistor.

49. A field electron emission device according to claim 48, wherein said resistor is applied as a resistive pad under each emitting patch.

50. A field electron emission device according to claim 49, wherein a respective said resistive pad is provided under each emitting patch, such that the area of each such resistive pad is greater than that of the respective emitting patch.

51. A field electron emission device according to any of claims 38 to 50, wherein said emitter material and/or a phosphor is/are coated upon one or more one-dimensional array of conductive tracks which are arranged to be addressed by electronic driving means so as to produce a scanning illuminated line.

52. A field electron emission device according to claim 51, including said electronic driving means.

53. A field electron emission device according to any of claims 38 to 52, wherein said environment is gaseous, liquid, solid, or a vacuum.

54. A field electron emission device according to any of claims 38 to 53, including a gettering material within the device.

55. A field electron emission device according to claim 54, wherein said gettering material is affixed to an anode of the device.

56. A field electron emission device according to claim 54 or 55, wherein said gettering material may be affixed to a cathode of the device.

57. A field electron emission device according to claim 56, wherein said field electron emission material is arranged in patches, and said gettering material is disposed within said patches.

58. A field electron emission device according to claim 54, comprising an anode, a cathode, spacer sites on said anode and cathode, spacers located at at least some of said spacer sites to space said anode from said cathode, and said gettering material located on said anode at others of said spacer sites where spacers are not located.

59. A field electron emission device according to claim 58, wherein said spacer sites are at a regular or periodic mutual spacing.

60. A field electron emission device according to any of claims 38 to 59, wherein a cathode of the device is optically translucent and so arranged in relation to an anode of the device that electrons emitted from the cathode impinge upon the anode to cause electro-luminescence at the anode, which electro-luminescence is visible through the optically translucent cathode.

61. A field electron emission device substantially as hereinbefore described with reference to the accompanying drawings.